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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 3 :		(11) International Publication Number: WO 86/ 06109
C30B 15/04	A1	(43) International Publication Date: 23 October 1986 (23.10.86)

(21) International Application Number: PCT/US85/00697

(22) International Filing Date: 16 April 1985 (16.04.85)

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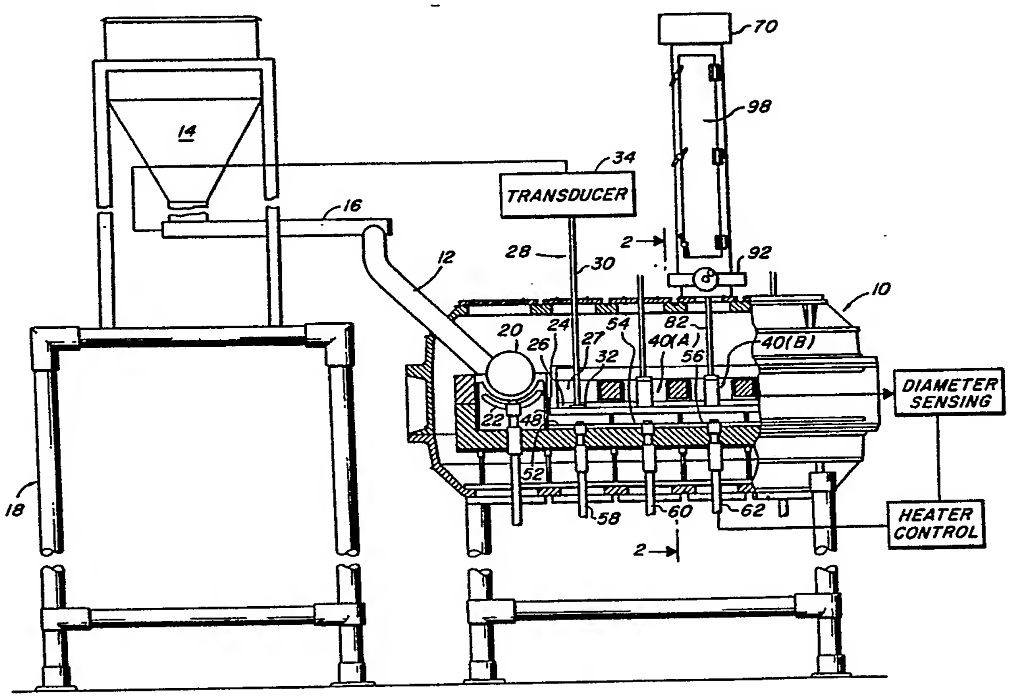
(81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent), DK, FI, FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent).

Published
With international search report.

(54) Title: METHOD AND APPARATUS FOR GROWING SINGLE CRYSTAL BODIES



(57) Abstract

A method and apparatus for use in growing single crystal bodies. The method includes directional solidification techniques in which a boule is pulled from a thermally controlled melt on a substantially continuous basis while the melt is continuously replenished from feed stock. The process is carried out in a vacuum and with or without a melt overflow. The apparatus includes a shallow through crucible (26), multiple pulling zones (40) and continuous silicon feed means (24) controlled by the melt level.

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METHOD AND APPARATUS FOR GROWING SINGLE CRYSTAL BODIES

BACKGROUND OF THE INVENTION

Typical metallurgical silicon contains from 0.5 to as much as 2 wt% impurities.

Efforts have been made to improve material of this quality by various treatments. These treatments have included various acid leaching schemes, molten solvent extractions and slagging. Improved grades of silicon metal with reduced impurity content have also been produced on a pilot scale by the use of purer raw materials and improved furnace practice. (See e.g. L. Hunt, V. Dosaj, J. McCormick and A. Raucholz, Proc. 13th IEEE Photovoltaic Spec. Conf., p. 333, 1978).

Typically, directional solidification of such treated feed material has been employed as a final step to take advantage of the partitioning of impurities into the liquid during solidification. The efficiency of this partitioning for a given impurity element is indicated by the so-called segregation coefficient which is simply the ratio of the solubility of the particular impurity in solid silicon to the solubility in liquid silicon at the melting point.

Knowledge of the effectiveness of this segregation process has made it a proven way to provide purification through some form of directional solidification in which impure starting material is melted and a boule of silicon is drawn from the melt, during which process a certain fraction of the impurities remain in the melt. The techniques and equipment associated with this purification approach thus far have been too expensive and have not proven to be particularly efficient in purifying the silicon. If all of the melt is solidified into the boule, a substantial section of the lower portion of the boule will contain an

unacceptable concentration of impurities and must be cut away as waste.

Heretofore, procedures of this nature were performed on a batch basis which was time consuming and expensive. Each batch required loading, melting, seeding, growing and cooling for each set up and involved about a day's time for each batch. In addition, a new crucible was required for each batch. On the average, about 25% of the available silicon was wasted by this method.

Accordingly, it is an object of the present invention to provide a novel method and associated apparatus for growing single crystal bodies.

SUMMARY OF THE INVENTION

The method of forming crystal bodies from materials such as silicon, comprises the steps of melting crystal forming material, delivering the same into a shallow temperature controlled crystal-forming crucible having a plurality of pulling zones, and maintaining the level of the melt therein by replenishment with fresh quantities of crystal-forming material. A seed placed on the surface of the melt is withdrawn in a directional solidification step.

When growing single crystals the process is carried out under a vacuum, using pure silicon feed material.

This invention also features an apparatus for growing single crystal boules therefrom on a substantially continuous basis. The apparatus includes a closed chamber having a shallow trough crucible with multiple pulling zones and feed melt replenishing means connected thereto and controlled by the level of the melt in the trough. For growing single crystals vacuum

means are provided for evacuating the chamber. Pulling equipment associated with the melt is adapted to pull boules vertically from the melt.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a view in front elevation, partly in section, of a combination crystal pulling and silicon purifying apparatus made according to the invention;

Fig. 2 is a cross-sectional view taken along the line 2-2 of Fig. 1;

Fig. 3 is a top plan view of the trough portion of the apparatus showing multiple pulling zones for boule formation;

Fig. 4 is a cross-sectional view taken along the line 4-4 of Fig. 3;

Fig. 5 is a detailed sectional view in side elevation showing one of the pulling stations of Figs. 3 and 4.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring now to the drawings, the reference character 10 generally indicates a housing for use in purifying relatively impure crystal-forming materials such as silicon as well as for pulling single crystal boules of silicon, or the like, from the melt thereof. The chamber 10 is connected by means of a duct 12 to a hopper 14, or the like, containing fragmented silicon or other such material. The hopper 14 connects to the duct 12 by means of a vibratory feeder 16, or similar dispenser.

The hopper 14 is mounted on a suitable frame 18 to position the hopper at a height above the housing 10 so that feed stock in the hopper may flow down through the duct 12 which

extends through a sealed opening in the wall of the housing 10 into a crucible 20 in which the feed stock is melted by heating elements 22. From the crucible 20 a melt feed 24 delivers molten silicon into a shallow trough 26, also located within the housing chamber. In practice, the housing 10 forms a sealed, air-tight chamber, which can be put under vacuum in order to eliminate or reduce silicon oxides which can interfere with single crystal growth or pressurized with an atmosphere of argon or the like when in a purifying mode.

The trough 26 is made out of a suitable material capable of withstanding the high heat involved in maintaining the silicon or the like in a molten state as well as not reacting with the silicon. For this purpose graphite with fused silica liners have been found satisfactory expecially for growing single crystal boules. The trough 26 includes a replenishment area 27 at one end thereof directly below the melt feed 24. In the replenishment area 27 there is a liquid level sensing device generally indicated by the reference character 28 which includes a stem 30 at the lower end of which is a float 32 adapted to ride on the surface of the melt. The stem 30 drives a transducer 34 which, in turn, provides a feed back signal to the vibratory feeder 16, turning the feeder on and off as necessary to maintain a substantially constant level of melt in the replenishment area. Various other level sensing devices may be used such as optical detectors, mechanical feelers, and the like. Preferably the level control area should be spaced somewhat from the replenishment area and protected as by a barrier 29 (Fig. 3) to prevent the generation of false signals by disturbances of the melt surface from replenishment material entering the trough through the melt feed 24.

The trough is also formed with a plurality of crystal growing areas 40 (a), (b) etc., preferably arranged in a row

lengthwise of the trough 26. The trough typically is in the form of an elongated rectangle having a bottom wall 42, low sidewalls 44 and 46 and end walls 48 and 50. Below the bottom wall 42 independent heating elements 52, 54, 56 etc. are disposed, one underneath the replenishment area and one under each growing area. The heating elements are energized by means of electrical cables 58, 60, 62 etc.

Each growing area 40 is located within an enclosure defined by walls 64 defining a generally square area along the centerline of the trough. The walls 64 are formed with openings 66 and 68 at opposite sides thereof to allow the flow of melt through the zone. Each growing area is thermally isolated from adjacent growing areas by suitable means such as double side walls 65 separated by a space therebetween. Within each enclosure there is provided a sub-surface thermal stabilizing disc 67 (Fig. 5) generally corresponding with the diameter of a boule 69 being drawn from the growing zone. The stabilizing disc 67 serves to stabilize the shape of the boule as it is drawn vertically upwards by means of a pulling mechanism well known in the art and generally indicated by reference character 70. Above each zone and slightly spaced from the surface of the melt is a radiation shield 72 of an annular configuration having an inside diameter generally corresponding with the diameter of the stabilizing disc 67. The function of the shield 72 is to control radiational heat loss outwards of the boule so that the melt around the outer portion of the zone remains in a liquid state. The melt delivered by the melt feed 24 into the trough will flow along a feed channel 74 on the side of the trough with fresh melt entering into each growing zone through its wall opening 66 to form a shallow pool of melt, preferably, 1" or less deep. Excess melt will flow out of the opposite opening 68 into a drain channel 76 formed along the opposite side of the trough. The drain channel leads to an overflow weir 78 which, when used,

continuously carries away from the trough impurities which would otherwise increase in concentration in the melt. Typically, the overflow weir 78 is designed to carry off about 10% of the melt and preferably is taken by an overflow arrangement at the melt surface.

The overflow control preferably is in the form of a weir wall having a notch in its upper edge and is used when the equipment is in the purification mode, but is removed, blocked off or otherwise disabled when the equipment is in the single crystal growing mode, using high purity feed. A drain tube 79 beyond the weir 78 carries away the overflow. Other means for continuously removing a portion of the melt can be provided. For example, instead of the drain arrangement shown, another boule forming station could be provided to form a boule from the impure melt.

Whether the directional solidification process is carried out to form poly-crystalline or single crystal boules, the trough utilized should be shallow. It has been found that it is easy to control solidification and crystal growth from a melt in a shallow trough as opposed to deep trough since the shallow trough substantially reduces effects due to convection currents in the melt. Using a shallow trough, thermal isolation of adjacent growing zones and an independent puller associated with each growing area, maximum control is achieved since the large thermal mass characteristic of the melt commonly used in a large Czochralski system is not present.

A simple optical system providing feedback to control the independent heaters is one means for controlling the boule diameter while the crystal pull rate is kept steady.

Compared to conventional systems, the reseeding time involved in the directional solidification method and apparatus

as disclosed herein is at a minimum, since approximately 95% of the possible pulling time available is productively utilized. With a conventional system a significant amount of time is lost in reseeding since it is necessary to melt new feed materials, then seed and finally neck the end product. By providing a continuous feed, with or without a continuous 10% overflow, no time is lost in replenishment thereby providing a very consistent product, whereas in a conventional system there is a substantial amount of down time as new feed is prepared. Also, the purity of the product varies at different parts thereof because of changing concentrations of impurities. Using a low volume shallow trough crucible it is possible to achieve continuous production of several boules with independent control over the formation of each boule and involving low capital cost per boule.

In a single production batch procedure, a long down time is involved in melting the feed stock and, typically, each boule requires a relatively high capital cost. Using fused silica liners in the crucible it is possible to operate on a substantially continuous basis up to a week using one fused silica liner. In a batch process the crucible must be replaced after each batch and a significant part of down time is involved in setting up for each cycle. This results in a substantial amount of lost growing time as compared to the present invention. By having the multiple boule pulling capability,a single housing unit involving relatively small incremental capital cost may be used, as opposed to a single ingot production which requires a relatively high capital cost per boule.

As shown in Fig. 4, each pulling station is equipped with its own pulling machanism 70 carried on a tower 80 mounted on the top of the chamber above each growing area 40. Each tower is of a height sufffcient to accomodate a full length boule, typically 4' and perhaps 6 - 8" in diameter pulled from the

trough by means of a rod 82 (Fig. 2), or the like, extending from mechanism 70 down through the tower into the chamber 10. A seed holder 84 is attached to the lower end of the rod and is adapted to be moved down to the melt surface and then pulled upwards as the boule forms.

When the apparatus is used in the single crystal forming mode, the chamber is evacuated by opening a valve 86 to a vacuum source 88 and the procedure is carried out under a low or partial vacuum. A trough with quartz liner is employed and the overflow wier is not utilized. (If the apparatus is in the purifying mode, the overflow weir is used and instead of a vacuum, the chamber is charged with an atmosphere of inert gas such as argon by opening a valve 90.) When growing a single crystal the starting material should be purer than the starting material used in the purification process (metallurgical grade silicon).

When a boule has been grown to its intended length, it is drawn up out of the melt and into its respective tower. The tower is then sealed off from the chamber 10 by closing a gate valve 92 located at the lower end of each tower. The vacuum in the tower can be broken or the argon pressure relieved by opening a valve 94 in a vent line 96. Thereupon, an elongated door 9B extending substantially the full length of each tower may be opened to permit removal of the boule and reseeding of the seed holder. Once reseeded, the vent valve 94 is closed, the door 98 is closed and locked, the tower evacuated or charged with argon, as required, the gate valve 92 opened and the seed holder lowered to the melt surface for another growing cycle.

The continuous replenishment of the melt not only permits more efficiency in either mode of operation, it also allows for uniform doping of the material in the single crystal

growing mode. The close thermal control over each growing station contributes to an end product of consistent high quality. The thermal control reduces the effects of changes in growth speed and defect formation.

While the invention is particularly useful with respect to the processing of silicon, it can be used advantageously with other crystal material that melts congruently and, in general, any material that can be grown by the Czochralski method and equipment can be processed by the method and apparatus disclosed herein. Those elements and compounds handled most easily are characterized by a low vapor pressure, typically 1/10 of an atmosphere or less. For materials having higher vapor pressures, special means would be required to contain the material.

While the invention has been described with particular reference to the illustrated embodiments, numerous modifications thereto will appear to those skilled in the art.

Having thus described the invention, what I claim is:

1. A method of growing a single crystal body from a melt thereof, comprising the steps of:

(a) heating crystal-forming material to form a melt thereof,

(b) delivering said melt to an evacuated crystal growing zone on a substantially continuous basis to form a shallow pool thereof,

(c) applying a crystalline seed to the surface of said melt in said zone and removing a single crystalline body therefrom at a rate equal to the rate of crystallization of said melt, and,

(d) controlling the temperature of the melt in said pool for maintaining an equilibrium between crystal growth and melt replenishment.

2. The method of claim 1 wherein said seed is withdrawn vertically from said melt to form a boule thereby.

3. The method of claim 1 including the step of applying at least one dopant selectively to said melt on a substantially continuous basis.

4. The method of claim 1 wherein said melt is an element selected from the group consisting of silicon and germanium.

5. Apparatus for growing a single crystal body from a melt thereof comprising:

(a) walls defining a chamber,

(b) container means in said chamber

adapted to contain quantity of said melt,

(c) melt replenishment means operatively associated with said container means for replenishing said melt on a substantially continuous basis,

(d) vacuum means operatively associated with said chamber for maintaining a vacuum in said chamber, and,

(e) pulling means operatively associated with said chamber for pulling a single crystal body from said melt on a substantially continuous basis.

6. Apparatus according to claim 5 wherein said container means includes a shallow trough.

7. Apparatus according to claim 6 wherein said trough includes a plurality of separate crystal growing zones communicating with said melt replenishment means, and individual pulling means operatively associated with each of said zone whereby a plurality of single crystal bodies can be pulled simultaneously from a single trough.

8. Apparatus according to claim 7 including individual heating means operatively associated with each of said zones.

9. Apparatus according to claim 7 wherein said pulling means is mounted above each of said zones for pulling a single crystal boule from each of said zones vertically from said melt in each zone.

10. Apparatus according to claim 8 including a stabilizing ring mounted in each zone below the surface of the

melt for controlling the diameter of the boule drawn therefrom, and an annular radiation shield mounted concentrically to said ring and above the melt surface, said shield having an inside diameter greater than the diameter of the boule drawn therethrough.

11. Apparatus according to claim 5 wherein said walls define a second chamber connected to and communicating with said first chamber and connected to said pulling means, said second chamber adapted to receive said single crystal body pulled by said pulling means from said melt, closure means connected to said second chamber for providing access thereto and isolation means connected to said second chamber for selectively isolating said second chamber from said first chamber.

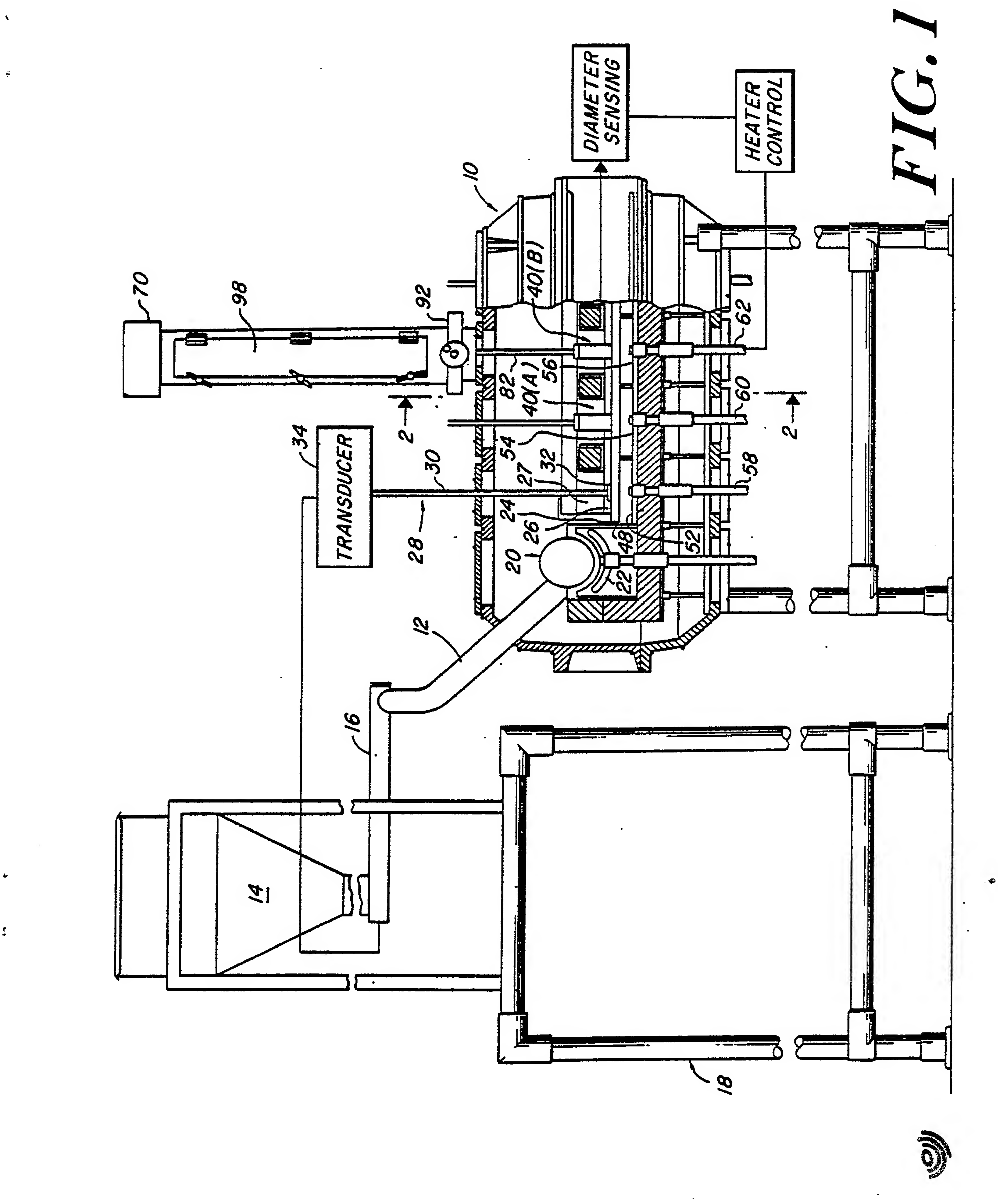
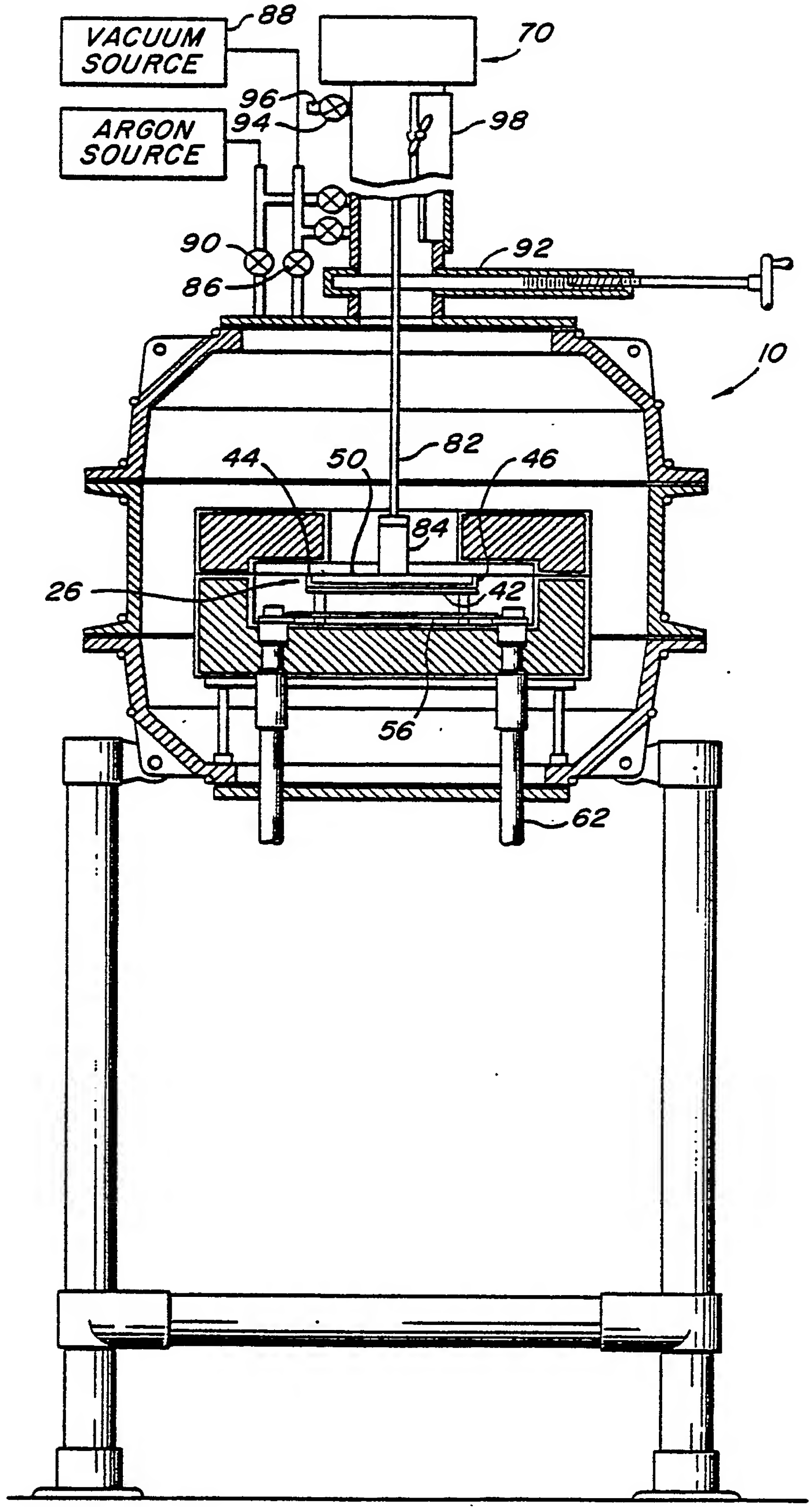


FIG. 1



VACUUM SOURCE
ARGON SOURCE
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94
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92
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44
50
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84
26
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56
62

FIG. 2

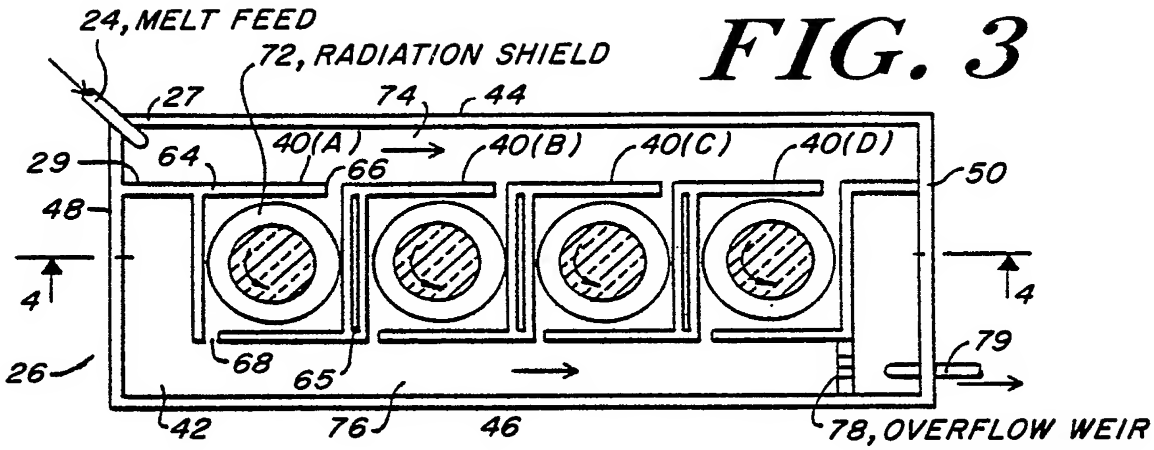

FIG. 3

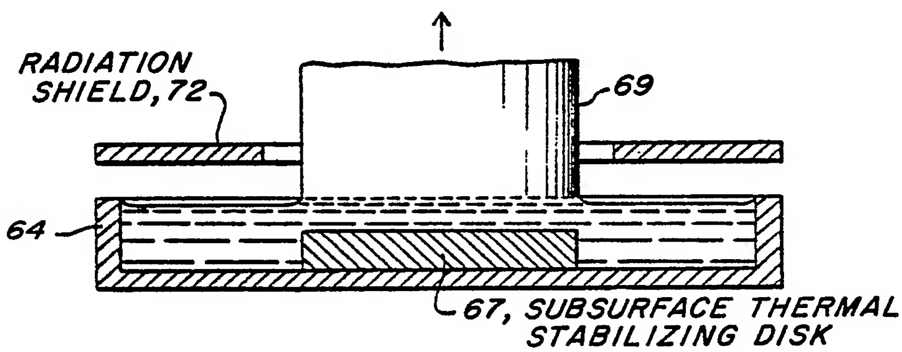

FIG. 5

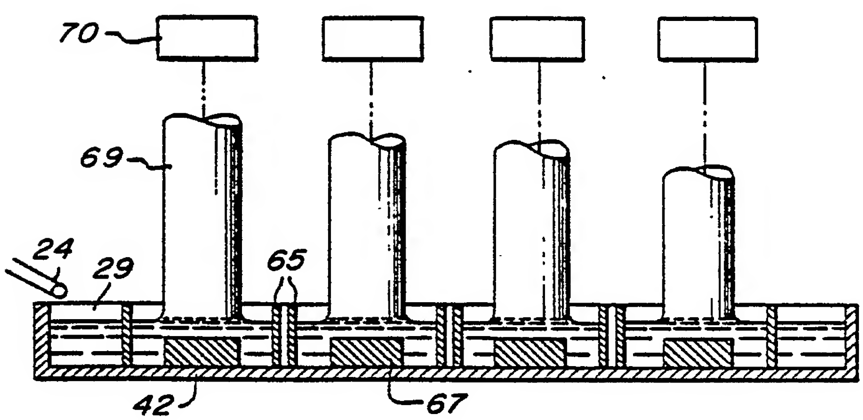

FIG. 4

INTERNATIONAL SEARCH REPORT

International Application No PCT/US85/00697

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

U.S. CL. 156/617 sp;422/249
INT. CL.[3] C30B 15/04

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
U.S.	156/608, 617R, 617sp, DIG 64, DIG 67, DIG 89, DIG 98 422/246, 247, 249;423/348

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
A	U.S., A, 4,225,378, PUBLISHED 30 SEPTEMBER 1980, GARRISON	1,2,4-7,9,11
A	U.S., A. 2,727,839, PUBLISHED 20 DECEMBER 1955, SPARKS	1-7, 9
A	U.S., A, 4,410,494, PUBLISHED 18 OCTOBER 1983, FIEGL	1,2,4,5,7,8
A	U.S., A, 4,454,096, PUBLISHED 12 JUNE 1984, LORENZINI, ET AL.	1,2,4,5,7,8
A	U.S., A, 3,505,025, PUBLISHED 07 APRIL 1970, DESSAUER	1,2,4-7
A	U.S., A, 3,582,287, PUBLISHED 01 JUNE 1971, CAPITA	1-6
A	U.S., A, 2,876,147, PUBLISHED 03 MARCH 1959, KNIEPKAMP, ET AL.	1,2,4,5
A	U.S., A, 2,892,739, PUBLISHED 30 JUNE 1959, RUSLER	1-5
A	U.S., A, 3,206,286, PUBLISHED 14 SEPTEMBER 1965, BENNETT, JR., ET AL.	1,2,4,5
A	U.S., A, 3,507,625, PUBLISHED 21 APRIL 1970, DEYRIS	1-5

* Special categories of cited documents: [15]
"A" document defining the general state of the art which is not considered to be of particular relevance
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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
03 JUNE 1985	18 JUN 1985
International Searching Authority [1]	Signature of Authorized Officer [20]
ISA/US	MICHAEL S GZYBOWSKI BARRY S RICHMAN SUPERVISORY PATENT EXAMINER ART UNIT 134

Form PCT/ISA/210 (second sheet) (October 1981)

BAD ORIGINAL

International Application No. PCT/US85/00697

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

A	U.S., A, 4,036,595, PUBLISHED 19 JULY 1977, LORENZINI, ET AL.	1,2,4,5
A	U.S., A, 4,330,359, PUBLISHED 18 MAY 1982, SHLICHTA, ET AL.	1,2,4,5
A	U.S., A, 4,330,362, PUBLISHED 18 MAY 1982, ZULEHNER	1,2,4,5

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE [10]

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1.☐ Claim numbers because they relate to subject matter [12] not required to be searched by this Authority, namely:

2.☐ Claim numbers because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out [13], specifically:

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING [11]

This International Searching Authority found multiple inventions in this international application as follows:

1.☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2.☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3.☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4.☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.